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FTIR Photoacoustic Spectroscopy of Diesel Lubricant Oils Containing Particulate Matter

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Technical Paper

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Monitoring of engine lubricants in service is important for evaluating engine conditions as well as the performance of new and existing lubricant formulations. Fourier-transform infrared (FTIR) spectroscopy has previously been demonstrated as an effective technique for analyzing lubricant condition, but used oils laden with soot and other particulate matter are difficult to analyze with common FTIR sampling techniques because of the strong light absorption and scattering by the particulates. FTIR photoacoustic spectroscopy is examined here as an alternative sampling technique for analyzing particulate-laden oils. Diesel-engine oils spiked with carbon black and phorone are analyzed quantitatively for particulate and carbonyl-species content using FTIR photoacoustic spectroscopy. Photoacoustics is found to be insensitive to the light scattering by particulate matter, but the strength of spectrum bands is reduced by the light absorption by particulate matter. A method is proposed to compensate for the loss of band strength so that quantitative measurements can be made.

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INTRODUCTION

Fourier-transform infrared (FTIR) spectroscopy has been used for many years to analyze engine crankcase oils and other lubricants for chemical degradation and contamination (Coates, 1986a, Coates, 1986b, Dong, Jefferies, Powell, Stellman). Both the loss of additives and the build up of decomposition products can be monitored over the lifetime of an oil (Coates, 1986a, Coates, 1986b, Dong, Powell, Stellman). Oxidation of the oil increases absorption in the 1650 to 1800 cm^{-1} region because of the production of carbonyl-containing species (Coates, 1986a, Coates, 1986b, Dong). Similarly, nitration increases absorption in the 1550 to 1650 cm^{-1} region (Coates, 1986b, Dong). Combining infrared spectroscopy with principal component analysis (PCA) can extend its analytical capability; PCA of infrared spectra has been used to create a metric for overall lubricant condition (Stellman), and to determine physical properties, such as viscosity (Stuart).

Attenuated total reflection (Jefferies, Powell, Wiseman) or short-path-length (typically 100 or 200 μm) transmission (Coates, 1986a, Coates, 1986b, Dong, Powell, Stuart) are the two sampling techniques that have been used for virtually all infrared spectroscopy of oils so far. Attenuated total reflection (ATR) has the potential advantage of ease of use. The sample can be pipetted or poured onto a horizontal ATR crystal, and then wiped off after testing. The very shallow probe depth of ATR (typically 1 or 2 μm, depending on wavelength and ATR-crystal material) allows it to acquire spectra even from oils containing high concentrations of suspended solids. Unfortunately, the shallow probe depth also makes ATR very susceptible to interference from contamination of the crystal, but ATR crystals are relatively

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soft so vigorous cleaning should be avoided (Powell). The small probe depth combined with the generally modest light throughput of ATR also limits its sensitivity so that low-concentration components may not be detected (Powell).

The longer effective path length in transmission, on the other hand, gives it substantial sensitivity and reduces its susceptibility to optical-element contamination, so it has often been the preferred sampling technique (Powell). Manually filling and cleaning a short-path-length transmission cell is difficult, especially with high-viscosity oils, thus a flow cell with a vacuum pump to pull samples and cleaning solvents through the cell is necessary for efficient testing. The greater effective path length of transmission spectroscopy makes it susceptible to problems from light scattering and absorption by suspended particulate matter in the oil. The presence of particulate matter both shifts the spectrum baseline because of panchromatic absorption and tilts it because of wavelength-dependent scattering. At moderate levels of particulate matter, the baseline tilt can be used as a measure of the particulate concentration (Powell). At higher levels, however, the oil becomes too opaque for accurate analysis.

The generally higher particulate loading in used diesel-engine oils makes them difficult samples for infrared analysis. This problem is likely to increase because exhaust-gas recirculation, which is being introduced to reduce NO_x emissions, tends to increase the production of particulate matter by diesel engines (Ladommatos ,1998a, Ladommatos, 1998b). What is needed is a sampling technique with an effective path length between that of ATR and the 100 μm or more used in transmission. Even better would be one with an effective path length that can be easily adjusted as needed without manipulating the sample. Photoacoustic spectroscopy (PAS) has just that property. In FTIR PAS, the probe depth, or effective path length, can be adjusted by changing the spectrometer scanning speed (McClelland, Rosencwaig). In PAS, the sample is sealed in a cell having a window and a microphone. Modulated light striking the sample heats the sample if it absorbs the light. This heat diffuses to the sample surface and warms the surrounding gas. The gas heating is modulated at the same frequency as the light, so the gas pressure inside the cell oscillates at this frequency, and the microphone senses this as sound. Because of this detection mechanism, PAS is largely unaffected by light scattering within a sample. It measures only the energy absorbed. Conventionally, the probe depth in PAS is identified with the thermal diffusion length, which is a measure of how far thermal waves can travel through a material. The thermal diffusion length, μ, is given by (Mc Clelland, Rosencwaig):

$$\mu = \left(\frac{D}{\pi f}\right)^{1/2} = \left(\frac{D}{\pi v \tilde{\nu}}\right)^{1/2} \qquad [1]$$

where D is the thermal diffusivity of the sample, f is the modulation frequency of the light and the thermal waves, v is the retardation (scanning) velocity of the FTIR spectrometer, and $\tilde{\nu}$ is the wavenumber of the light. The thermal diffusivity of mineral oil is 7.1 x 10^{-4} $cm^2 \cdot s^{-1}$ (Bartz). This means the thermal diffusion length increases from 4 μm to 38 μm at 1600 cm^{-1} as the FTIR scanning speed is reduced from 1 to 0.01 $cm \cdot s^{-1}$. On research-grade FTIR spectrometers, which have a wider range of scanning speeds, the maximum limit on the PAS probe depth is the optical opacity of the sample — how deeply the light beam penetrates. PAS also should offer advantages in oil-sample handling. Liquid samples are placed in a cup, which is then inserted into the cell. This should allow even highly viscous oils to be sampled. Because the sample does not contact any optical elements, contamination is eliminated, and if disposal sample cups are used, cleaning is eliminated.

The above considerations led to a survey of the efficacy of FTIR PAS for the analysis of used diesel-engine oil, which is reported here. This paper examines the ability of FTIR PAS to quantify the particulate loading in diesel oil and to quantify the amount of carbonyl-containing species in diesel oil whether or not particulate matter is present. Synthetically prepared samples containing known amounts of contaminants were tested instead of actual used-in-service oils so that the PAS results could be compared to reliable compositions.

EXPERIMENTAL

The FTIR PAS measurements were made using a Bio-Rad FTS 60A FTIR spectrometer with an MTEC Photoacoustics Model 200 photoacoustic detector. Spectra were collected at 8 cm^{-1} resolution by co-adding 256 scans at a 2.5 kHz scanning speed (0.16 $cm \cdot s^{-1}$ retardation velocity), corresponding to a 9 μm thermal diffusion length at 1600 cm^{-1}. Typical routine-analysis spectrometers can scan at speeds equal to or near this. A volume of 100 μL of each sample was pipetted into a 3-mm-deep stainless steel sample cup. The sample cups were 10.5 mm in diameter so that they just fit in the 11 mm-diameter sample holder of the detector. The sample cup rested on a 1.5 mm thick spacer that was atop a second 3-mm-high sample cup containing magnesium perchlorate desiccant. Zero grade helium gas was used to purge and fill the detector sample cell. Spectra were normalized with the spectrum of a glassy-carbon reference sample from MTEC Photoacoustics. The glassy carbon was placed atop the 1.5 mm spacer without a sample cup. The photoacoustic-detector amplifier gain was 32 for all spectra. Although all spectra in this paper are plotted on an arbitrary ordinate scale, the same arbitrary scale, where 100 corresponds to a signal equal to that of the glassy-carbon reference, is used throughout, so data from the various figures may be compared.

Samples were prepared by adding known weights of carbon lampblack (Fisher) and phorone (Aldrich), $((CH_3)_2C{=}CH)_2C{=}O$, to clean diesel oil. The lampblack and phorone were surrogates for particulate matter and for carbonyl-containing species indicative of oxidative degradation. The lampblack and phorone were dispersed in the oil by hand shaking a small vial containing the weighed components and glass beads. Because the lampblack slowly settled out of the

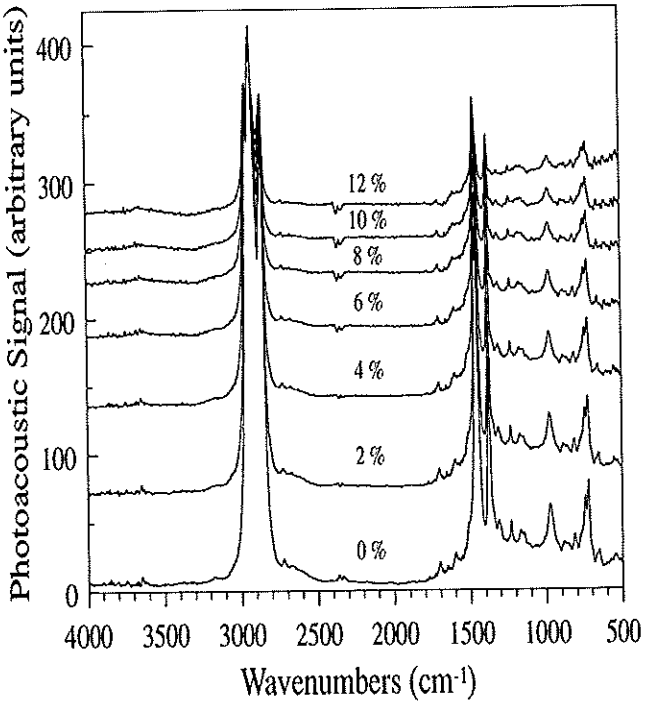

Fig. 1—FTIR photoacoustic spectra of diesel-engine oils containing carbon black at the weight percent levels indicated. All spectra are shown on the same ordinate scale.

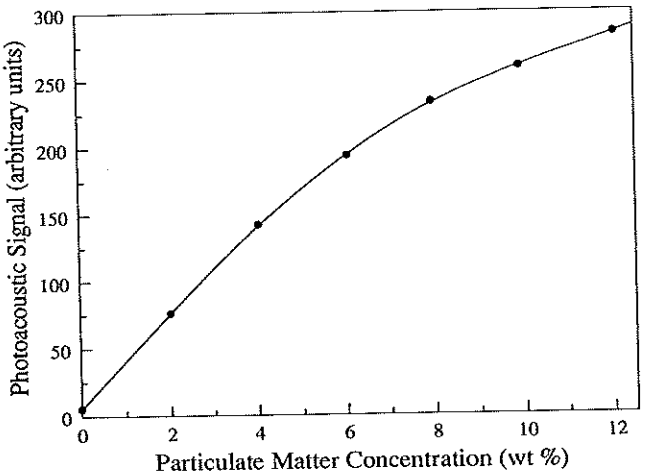

Fig. 2—Average signal level between 2000 and 2200 cm^{-1} for the spectra shown in Fig. 1 plotted as a function of the amount of particulate matter (carbon black) present in the sample.

oil, each sample was shaken just before the 100 μL aliquot was drawn. Nevertheless, settling may introduce a small error. The volatility of phorone is low (51 Pa at 20°C), so the loss of phorone from the samples and the contribution by headspace gases to the photoacoustic signal are negligible.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR PAS spectra for a series of oil samples containing various amounts of carbon-black particulate matter ranging from 0 to 12 wt. %. The spectra, which are plotted on a common scale, show that a rising baseline is the primary effect of increasing particulate concentration. The relatively horizontal baselines indicate that light scattering is not a strong factor in these spectra, unlike in transmission spectra. Figure 2 shows the correlation between the height of the baseline and the amount of particulate matter in the oil. The quantity plotted is the average value of the spectrum baseline over the 2000 to 2200 cm^{-1} range. The nonlinearity of the curve is common in FTIR PAS data for strong absorptions. The shape of the curve shows the gentle onset of saturation with increasing absorption that is typical in FTIR PAS (McClelland). The curve indicates that full signal saturation, where the line becomes horizontal and the particulate-matter concentration can no longer be determined, will not occur until considerably higher concentrations than those plotted, which is probably higher than would be of interest due to viscosity considerations. The onset of the curvature in the plot could be shifted to higher particulate concentrations by acquiring spectra at a higher scanning speed. As Eq. [1] shows, this would reduce the thermal diffusion length and reduce the observed absorption level at a given particulate level.

Figure 1 also shows a secondary effect that particulate matter has on the spectra. As the concentration of particulates increases, the sizes of the various oil absorption bands decrease. All of the oil bands within one spectrum, ranging from the strongest C-H-stretch band at 2930 cm^{-1} to the weak structure in the fingerprint region, are reduced by the same proportion. Figure 3 is a plot of the size of the oil bands relative to those in the particulate-free oil as a function of the height of the baseline (i.e., the ordinate values plotted in Fig. 2). The relative heights of the oil bands were determined subjectively by subtracting the particulate-free oil spectrum times a weighting factor from the other Fig. 1 spectra. The relative oil-band heights are the weighting factors that produced the cleanest subtraction spectra. The straight line in Fig. 3 is a linear regression of the data points and is given by the equation

$$R = 1.026 - 0.00264\ B \qquad [2]$$

where R is the relative oil-band height and B is the baseline height. Such a regression based on spectra of actual used oils would provide a calibration for the particulate-matter concentration in the oils. Extrapolating this line gives an abscissa intercept of 389. A signal level of 389 should therefore be the maximum possible signal level (i.e., the signal at complete saturation) for samples having the same thermal properties as the oil samples under the instrumental conditions used here. The height of the 2930-cm^{-1} band is a virtually constant 412 ± 1 for the 0- through 6-wt.-% spectra in Fig. 1, which suggests that the band is completely saturated. The height of the 2930-cm^{-1} band drops off slightly as the

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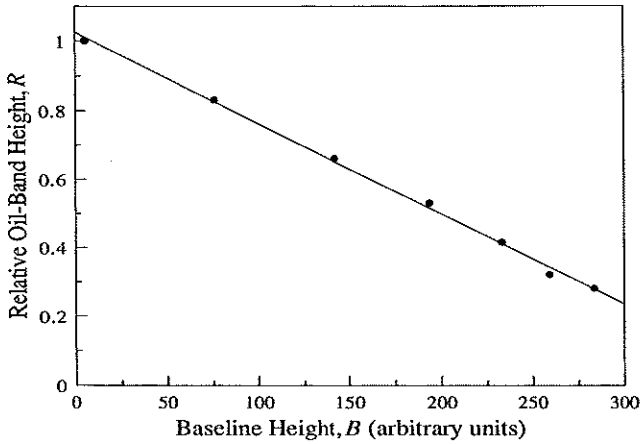

Fig. 3—Heights of the oil absorption bands of the spectra in Fig. 1 shown as a function of the spectrum-baseline height (average signal between 2000 and 2200 cm^{-1}), which rises as the concentration of carbon black increases. Band heights are plotted on a relative scale in which the band heights for the carbon-black-free oil are set to 1.

particulate concentration continues to rise, which suggests that the thermal properties of the carbonblack-laden oil above 6 wt. % may differ measurably from that of the clean oil. The difference between 389 and 412 is probably not significant, given the accuracy of the extrapolation of the line in Fig. 3, but interestingly, a linear regression based on only the 0- through 6-wt.-% spectra (which gives R = 1.016 - 0.00250 B) has an abscissa intercept of 406, in substantial agreement with the observed 2930-cm^{-1}-band height for those spectra.

The bottom panel of Fig. 4 shows spectra of clean diesel oil to which various concentrations of phorone have been added. The ordinate scale is marked for the 0 wt. % spectrum and the other spectra have been offset vertically for clarity. The phorone bands that are obvious at the 5 wt. % level are small but already distinct even at the 0.7 wt. % level. The upper panel of Fig. 4 shows a similar set of spectra for phorone spiked in diesel oil, but here, all of the oils also contain 3.9 wt. % carbon black. As in the lower panel, the ordinate scale is for the 0 wt. % spectrum and the other spectra are offset. As noted for the Fig. 1 spectra, the presence of the carbon black does two things; the baseline is raised, and the strengths of the various absorption bands are all reduced relative to the carbon-black-free spectra. Figure 5 plots the height of the 1634 cm^{-1} carbonyl band of phorone for two series of samples as a function of the phorone concentration. The open circles are for samples containing no carbon black and the black circles are for samples containing 3.9 wt. % carbon black. The two lines are linear regressions of the data points; they have slopes of 28.3 for the clean oil and 24.0 for the carbon-black-containing oil. The baseline heights of the 3.9 wt. % carbon-black spectra used for Fig. 5 give a value of 0.67 ± 0.02 for R in Eq. [2]. This does not equal the ratio of the two Fig. 5 slopes, which is 0.85. The oil bands and the phorone bands are not reduced by the same fraction by the presence of carbon black. Apparently, calibrations like Eq.

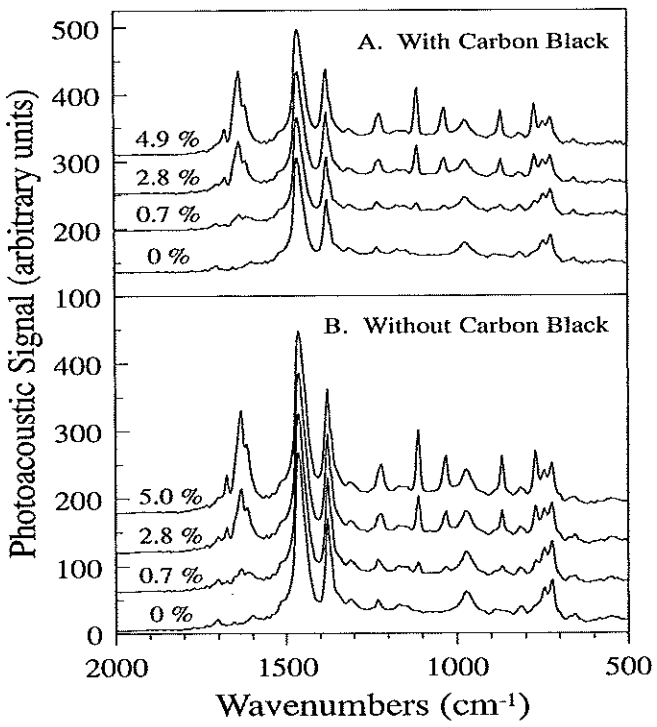

Fig. 4—Spectra of diesel-engine oils containing phorone at the weight percent levels indicated and (a) containing 3.9 wt. % carbon black or (b) containing no carbon black.

[2] must be done separately for each component analyzed, but once produced, they can compensate for the effects of particulates.

Spectral subtraction is a valuable means of observing small changes in PAS spectra. It could be used to isolate features arising from the degradation or contamination of oil by subtracting off the spectrum of clean, unused oil. Figure 6 illustrates this possibility. The bottom panel of Fig. 6 shows spectra of phorone generated by subtracting the spectrum of clean oil, the bottom-most spectrum in Fig. 4, from the other spectra in the lower panel of Fig. 4, with a 1:1 weighting. A spectrum of neat, liquid phorone is shown at the top of Fig. 6 for comparison. All of the phorone bands are present in the subtraction spectra in the bottom panel of Fig. 6. The phorone bands at 1385 and 1445 cm^{-1}, which are completely obscured prior to the subtraction by the much stronger oil bands at 1375 and 1460 cm^{-1}, are observable even at the 0.7 wt. % level. The middle panel of Fig. 6 demonstrates the same thing for the spectra in the bottom panel of Fig. 6 demonstrates the same thing for the spectra of oils with 3.9 wt. % carbon black. The clean oil (no phorone or carbon black) spectrum was subtracted from each of the spectra in the upper panel of Fig. 4 with a weighting of R:1, where R is given by Eq. [2]. As previously mentioned, this gives R = 0.67 ± 0.02 for these spectra. All of the small oil bands have been completely removed from the subtraction spectra, but this time a little negative residue of the 1375 and 1460 cm^{-1} oil bands is still present, which is enough to obscure the overlapping phorone features at 0.7 wt. %. The other phorone bands, however, are clearly present.

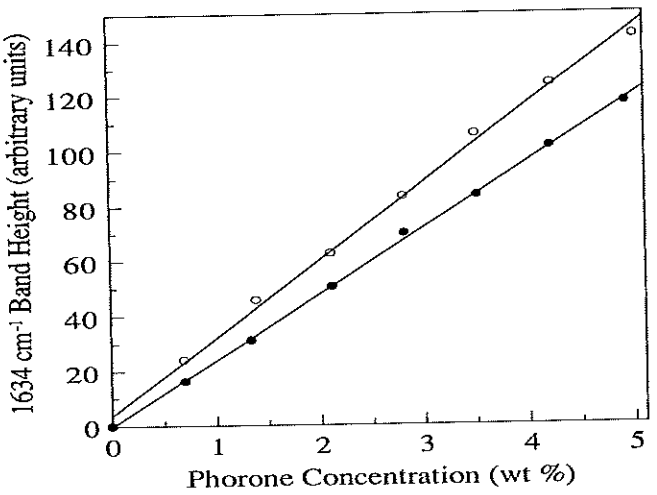

Fig. 5—Height of the 1634 cm^{-1} carbonyl band of phorone as a function of phorone concentration in oils containing 3.9 wt. % carbon black (•) and no carbon black (○).

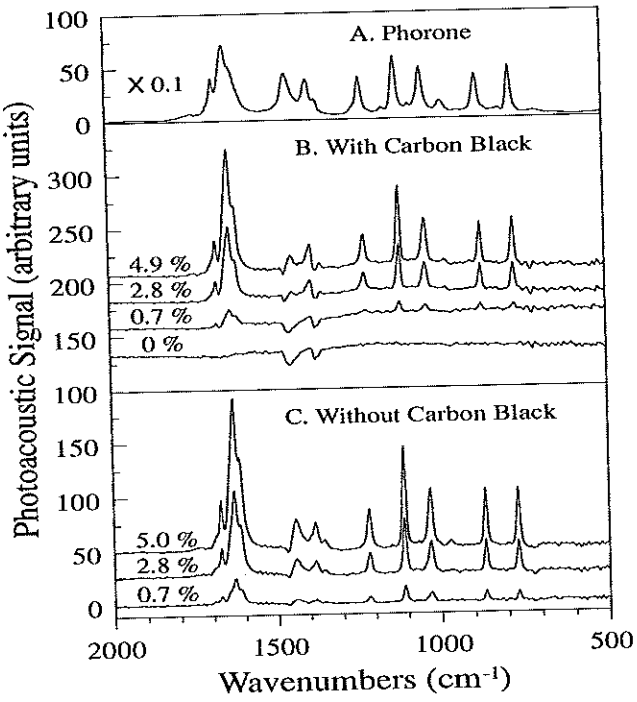

Fig. 6—Difference spectra generated by the weighted subtraction of the spectrum of clean oil from the spectra of oil containing the indicated weight percent of phorone and (b) 3.9 wt. % carbon black or (c) no carbon black. (A) FTIR photoacoustic spectrum of neat, liquid phorone provided for comparison.

CONCLUSION

FTIR PAS measurements on particulate-laden used-oil surrogates show good quantitative capabilities for both particulate loading and carbonyl-species concentrations. Spectral subtractions can be readily done on spectra of oils containing particulate matter using the methods described in this work. These spectral measurement and manipulation capabilities combined with its ease of use should make FTIR PAS a useful tool for molecular analysis of in-service diesel and other engine oils.

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